

WHAT IS CLAIMED IS:

1. A hetero-branched radial polystyrene-polyisoprene block copolymer represented by

5 (pS-pI)₃X-(pB-pI-pS)

wherein pS is polystyrene; pI is polyisoprene; pB is polybutadiene; and X is a residue of a tetravalent coupling agent.

2. The hetero-branched radial polystyrene-polyisoprene block copolymer as
10 claimed in claim 1, wherein a block represented by pS has a weight average molecular weight of 5,000 to 40,000; a block represented by pB has a weight average molecular weight of 50 to 40,000; and the block copolymer has a weight average molecular weight of 50,000 to 400,000.

15 3. The hetero-branched radial polystyrene-polyisoprene block copolymer as claimed in claim 1, wherein X is Si.

4. The hetero-branched radial polystyrene-polyisoprene block copolymer as
claimed in claim 2, wherein X is Si.

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5. A method for preparing a hetero-branched radial polystyrene-polyisoprene block copolymer, comprising:

(a) adding a styrene monomer in the presence of an organolithium initiator in an inert hydrocarbon solvent and proceeding polymerization until all of the styrene monomer
25 is consumed, to synthesize a polystyrene living polymer;

(b) adding an isoprene monomer to the polystyrene living polymer and proceeding polymerization until all of the isoprene monomer is consumed, to synthesize a living polystyrene-polyisoprene diblock polymer;

(c) adding a tetravalent coupling agent to the living polystyrene-polyisoprene
5 diblock polymer and proceeding a primary coupling reaction; and

(d) further adding a butadiene monomer, proceeding a secondary coupling reaction to produce a hetero-branched radial polystyrene-polyisoprene block copolymer represented by the following formula I while the butadiene monomer is consumed to form a butadiene block, and completing the reaction:



wherein pS is polystyrene; pl is polyisoprene; pB is polybutadiene; and X is a residue of the tetravalent coupling agent.

6. The method as claimed in claim 5, wherein the inert hydrocarbon solvent
15 includes cyclohexane, a mixture of cyclohexane and n-hexane, or a mixture of cyclohexane and n-heptane.

7. The method as claimed in claim 5, wherein the organolithium initiator includes n-butyllithium, or sec-butyllithium.

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8. The method as claimed in claim 5, wherein the tetravalent coupling agent includes at least one selected from halogenated silicon coupling agents such as silicon tetrachloride, or silicon tetrabromide; or alkoxyasilanes such as tetramethoxysilane, or tetraethoxysilane.

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9. The method as claimed in claim 5, wherein the butadiene monomer is added in an amount of 0.05 to 10 wt.%.

10. The method as claimed in claim 5, wherein the styrene monomer is added in
5 an amount of 10 to 50 wt.%.

11. The method as claimed in claim 5, wherein a block represented by pS has a weight average molecular weight of 5,000 to 40,000.

10 12. The method as claimed in claim 5, wherein the block copolymer has a weight average molecular weight of 50,000 to 400,000.

13. The method as claimed in claim 5, wherein the coupling rate after secondary coupling reaction is in the range of 30 to 100 %.

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14. The method as claimed in claim 5, further comprising:

adding a polar compound so as to control the rates of the polymerization and coupling reactions.

20 15. The method as claimed in claim 14, wherein the polar compound includes diethyl ether, dibutyl ether, THF, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, dioxane, triethylene glycol ether, 1,2-dimethoxy benzene, 1,2,3-trimethoxy benzene, 1,2,4-trimethoxy benzene, 1,2,3-triethoxy benzene, 1,2,3-tributoxy benzene, triethyl amine, tripropyl amine, tributyl amine, N,N,N',N'-tetramethyl ethylene diamine, N,N,N',N'-

tetraethyl ethylene diamine, 1,2-dimorpholinoethane, 1,2-dipiperidinoethane, and Sparteine, which are used alone or in combination.

16. The method as claimed in claim 14, wherein the addition of the polar
5 compound is performed in batch mixing at the initial step of reaction, or separately at the initial and a butadiene monomer addition step of reaction.

17. The method as claimed in claim 15, wherein the addition of the polar
compound is performed in batch mixing at the initial step of reaction, or separately at the
10 initial and a butadiene monomer addition step of reaction.